



CHEMISTRY

BOOKS - VIKRAM PUBLICATION (ANDHRA PUBLICATION)

THERMODYNAMICS

Solved Problems

1. Express the change in internal energy of a system when
 - 1) No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have ?

ii) No work is done on the system, but a amount of heat is taken out from the system and given to the surroundings.

What type of wall does the system have?

iii) w amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be?



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2. Two litres of an ideal gas at a pressure of 10 atm expands isothermally into a vacuum until its total volume is 20 litres. How much heat is absorbed and how much work is done in the expansion?



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3. Consider the same expansion, but this time against a constant external pressure of 1 atm.



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4. Consider the same expansion, to a final volume of 10 litres conducted reversibly.



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5. If water vapour is assumed to be a perfect gas, molar enthalpy change for vapouration of 1 mole of water at 1 bar and 100°C is 41 kJ mol^{-1} . Calculate the internal energy change when

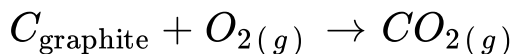
a) 1 mol of water is vapourised at 1 bar and 100°C

b) 1 mol of water liquid is converted into ice.



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6.1 g of graphite is burnt in a bomb calorimeter in excess of O_2 at 298 K and 1 atm. Pressure according to the equations.



During the reaction the temperature rises from 298 K to 200K. Heat capacity of the bomb calorimeter is 20.7KJK^{-1} . What is the enthalpy change for the above reaction at 298 K 1 atm?



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7. A swimmer coming out from a pool is covered with a film of water weighing about 18g. How much heat must be supplied to evaporate this water at 298 K? Calculate the internal energy of vaporisation at 100°C . ΔH_{vap}° for water at $373\text{K} = 40.66\text{kJmol}^{-1}$



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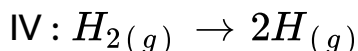
8. The combustion of one mole of benzene takes place at 298 and 1 atm. After combustion, $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation. $\Delta_f H^{\circ}$ benzene. Standard enthalpies of formation of $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ are $-393.5\text{ kJ mol}^{-1}$ and $-285.83\text{ kJ mol}^{-1}$ respectively.

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9. What are the sign of the entropy change (+ or -) in the following:

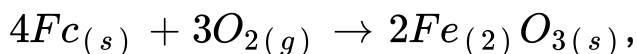
I : A liquid crystallises into a solid

II: Temperature of a crystalline solid is raised from 0K to 115K



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10. For the oxidation of iron



the entropy change is $-549.45 JK^{-1}mol^{-1}$ at 298 K.

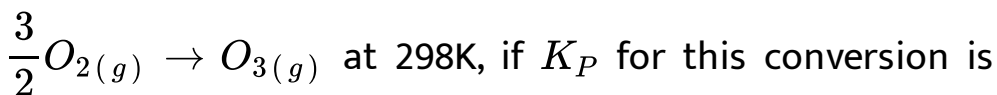
Though it has negative entropy change the reaction is spontaneous. Why?

$$\left(\Delta_r H^\theta = -164 \times 10^3 Jmol^{-1}\right)$$



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11. Calculate ΔG° for conversion of oxygen to ozone,



$$2.47 \times 10^{-29}$$



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12. Find out the value of equilibrium constant for the following reaction at 298 K.

$2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$ standard Gibbs energy change, ΔG° at the given temperature is $-13.6 \text{ kJ mol}^{-1}$.



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13. At 60°C dinitrogen tetroxide is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.



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Very Short Answer Questions

1. What is the information given by the terms thermodynamics?



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2. What is the relationship between the laws of thermodynamics and equilibrium state?



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3. Define a system. Give an example.



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4. The wall is adiabatic and $\Delta U = W_{ad}$. What do you understand about the heat and work with respect to the system?



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5. The system loses 'q' amount of heat though no work is done on the system. What type of wall does the system have?



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6. Express the change in internal energy of a system when
iii) w amount of work is done by the system and q amount

of heat is supplied to the system. What type of system would it be?



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7. What is the work done in the free expansion of an ideal gas in reversible and irreversible processes?



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8. From the equation $\Delta U = q - p_{ex}\Delta V$, if the volume is constant what is the value of ΔU ?



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9. In isothermal free expansion of an ideal gas find the value of q and ΔU .



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10. In isothermal irreversible change of ideal gas what is the value of q ?



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11. In isothermal reversible change of an ideal gas, what is the value of q ?



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12. For an adiabatic change of in an ideal gas what is the relationship between its ΔU and $W(\text{adiabatic})$?



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13. State the first law of thermodynamics. Explain its mathematical notation.



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14. What are the sign conventions of the work done on the system and work done by the system?



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15. Volume (V), Pressure (P) and Temperature (T) are state functions. Is the statement true?



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16. What are the heat (q) sign conventions when heat is transferred from the surroundings to the system and that transferred from system to the surrounding?



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17. No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have?



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18. No work is done on the system, but heat (q) is taken out from the system by the surroundings. What type of wall does the system have?



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19. Work is done by the system and heat (q) is supplied to the system. What type of system would it be?



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20. $q = w = -p_{ext}(v_f - v_i)$ is for irreversible.... Change.



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21. $q = -w = nRT \ln(v_f - v_i)$ is for isothermal change.



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22. What are the ' ΔH ' sign conventions for exothermic and endothermic reactions?



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23. What are intensive and extensive properties?



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24. In the equation $q = C \cdot \Delta \cdot m \cdot \Delta T$, if ΔT is change in temperature 'm' mass of the substance, and 'q' is heat required, what is 'C'?



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25. Give the equation that gives the relationship between ΔU and ΔH .



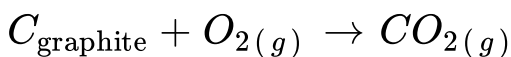
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26. What is the relationship between C_p and C_v ?



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27. 1 g of graphite is burnt in a bomb calorimeter in excess of O_2 at 298 K and 1 atm. Pressure according to the equations.



During the reaction the temperature rises from 298 K to 200K. Heat capacity of the bomb calorimeter is $20.7 K J K^{-1}$. What is the enthalpy change for the above reaction at 298 K 1 atm?

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28. For the above reaction what is the internal energy change, ΔU ?



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29. What is $\Delta_r H$ for $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O(l)$ in terms of molar enthalpies of the respective reaction and products?



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30. Enthalpy decreases is not the criterion for spontaneity. Why?



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31. Is increase of entropy the criterion for spontaneity ?
Why ?



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32. Explain the relationship between Gibbs energy change and equilibrium constant.



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33. If we measure ΔH^θ and ΔS^θ it is possible to estimate ΔG^θ . Is it true? Why?



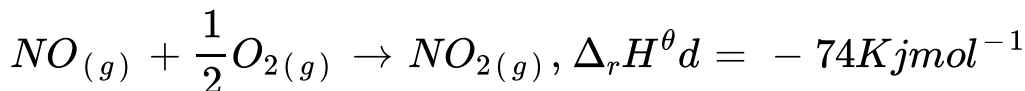
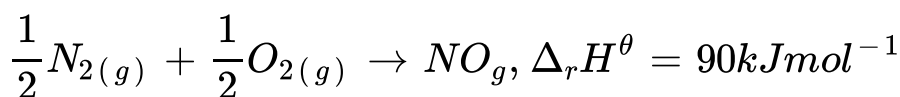
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34. Equilibrium constant 'K' is measured accurately in the laboratory at given temperature. Is it possible to calculate ΔG^θ at any other temperature ? How?



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35. Comment on the thermodynamics stability of $NO_{(g)}$ given that



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36. Calculate the entropy change in surroundings when 1.00 mole of $H_2O_{(l)}$ is formed under standard conditions $\Delta_f H^\theta = -286 \text{ kJ mol}^{-1}$.



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37. The equilibrium constant for a reaction is 10. What will be the value of ΔG ?

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, T = 300 \text{ K}.$$



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Short Answer Questions

1. State the third law of thermodynamics.



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2. What are open, closed and isolated systems ? Give one example for each.



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3. Define the state function and state variables. Give examples.



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4. "Internal energy is a state function." Explain.



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5. "Work is not a state function." Explain.



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6. What is heat? Explain.



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7. Derive the equation for ' W_{rev} ' in isothermal reversible process.



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8. Two litres of an ideal gas at a pressure of 10 atm expands isothermally into a vacuum until its total volume is 20 litres. How much heat is absorbed and how much work is done in the expansion?



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9. If the ideal gas given in the problem 45 expands against constant external pressure of 1 atm what is the q value?



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10. If the ideal gas given in the problem 45 expands to a final volume of 10L conducted reversibly what is q value?



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11. Explain the state function 'enthalpy, H'. What is the relationship between ΔU and ΔH ?



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12. Show that $\Delta H = \Delta U + \Delta n_{(g)} RT$



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13. If water vapour is assumed to be a perfect gas, molar enthalpy change for vapouration of 1 mole of water at 1 bar and 100°C is 41 kJ mol^{-1} . Calculate the internal energy change when

- a) 1 mol of water is vapourised at 1 bar and 100°C
- b) 1 mol of water liquid is converted into ice.



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14. Explain extensive and intensive properties.



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15. Define heat capacity. What are C_p and C_v ? Show that

$$C_p - C_v = R.$$



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16. Explain the determination of ΔU of a reaction calorimetrically.



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17. Explain the determination of ΔH of a reaction calorimetrically:



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18. What is enthalpy of a reaction? Explain the standard enthalpy of a reaction.



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19. What is the standard enthalpy of formation? Explain it with example.



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20. Define and explain enthalpy of phase transformation.



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21. Define and explain the standard enthalpy of vapourisation (Molar enthalpy of vapourisation).



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22. Define and explain the standard enthalpy of vapourisation (Molar enthalpy of vapourisation).

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23. Define and explain the standard enthalpy of vapourisation of sublimation.

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24. Define and explain the standard enthalpy of formation ($\Delta_r H^\theta$).





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25. State and explain the Hess's law of constant heat summation.



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26. Define and explain the enthalpy of combustion $(\Delta_c H^\theta)$.



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27. Define and explain the enthalpy of atomisation $(\Delta_a H^\theta)$.

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28. Define and explain the bond enthalpy ($\Delta_{\text{bond}}H^\theta$).

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29. What is the bond enthalpy of C-H bond of CH_4 ?

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30. Define heat of solution ($\Delta_{\text{sol}}H^\theta$) and heat of dilution.

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31. Define ionisation enthalpy and electron affinity.



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32. Explain the spontaneity of a process.



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33. Is decrease in enthalpy a criterion for spontaneity?

Explain.



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34. What is entropy? Explain with examples.



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35. Is increases in entropy a criterion for spontaneity? Explain.



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36. Can ΔU and ΔS discriminate between irreversible and reversible process? Explain.

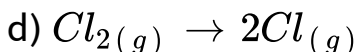


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37. In which of the following process entropy increases?

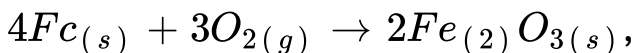
a) A liquid evaporates to vapour.

b) Temperature of a crystalline solid lowered from 115 K to 0 K.



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38. For the oxidation of iron



the entropy change is $-549.45 JK^{-1}mol^{-1}$ at 298 K.

Though it has negative entropy change the reaction is spontaneous. Why?

$$\left(\Delta_r H^\theta = -164 \times 10^3 Jmol^{-1} \right)$$

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39. Which formulate in the following are correct?

a) $G = H - TS$

b) $\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$

c) $\Delta S_{\text{surr}} = \frac{\Delta H_{\text{surr}}}{T} = \frac{-\Delta H_{\text{sys}}}{T}$

d) $\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \frac{(-\Delta H_{\text{sys}})}{T}$

e) $\Delta S_{\text{total}} = T\Delta S_{\text{sys}} - \Delta H_{\text{sys}}$

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40. Calculate $\Delta_r G^\theta$ for conversion of oxygen to ozone

$\frac{3}{2}O_{2(g)} \rightarrow O_{3(g)}$ at 298 K. K_p for the reaction is 2.43×10^{-29} .



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41. State the second law of thermodynamics and explain it.



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42. State the third law of thermodynamics.



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43. What is entropy? Explain with examples.



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44. Explain spontaneity of a process in terms of Gibbs energy.



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45. The sign and magnitude of Gibbs energy change of a chemical process tells about its spontaneity and useful work that could be extracted from it. Explain.

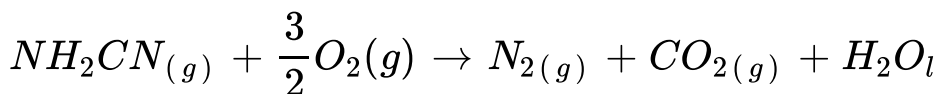


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46. In a process 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

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47. The reaction of cyanamide (s), with dioxygen was carried out in a bomb calorimeter and ΔU was found to be $-742.7 \text{ kJ mol}^{-1}$ at 298 K. Calculate the enthalpy change for the reaction at 298 K.

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48. Calculate the number of kJ of heat necessary to rise the temperature of 60.0 g of aluminum from $35^\circ\text{C} \rightarrow 55^\circ\text{C}$. Molar heat capacity of aluminum is $24 \text{ J mol}^{-1}\text{K}^{-1}$.

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49. Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to ice at -10.0°C .

$$\Delta_{\text{fus}}H = 6.03\text{kJmol}^{-1}\text{ at }0^{\circ}\text{C}$$

$$C_p[\text{H}_2\text{O}(l)] = 75.3\text{Jmol}^{-1}\text{K}^{-1}$$

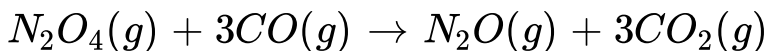
$$C_p[\text{H}_2\text{O}(s)] = 36.8\text{Jmol}^{-1}\text{K}^{-1}$$

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50. Enthalpy of combustion of carbon to CO_2 is -393.5kJmol^{-1} . Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.

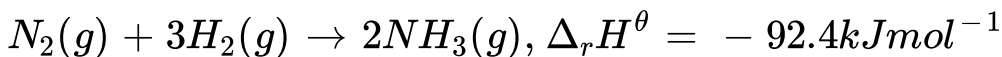
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51. Enthalpies of formation of $\text{CO}(g)$, $\text{CO}_2(g)$, $\text{N}_2\text{O}(g)$ and $\text{N}_2\text{O}_4(g)$ are -110 , -393.81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction:



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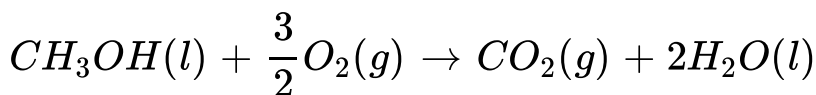
52. Given



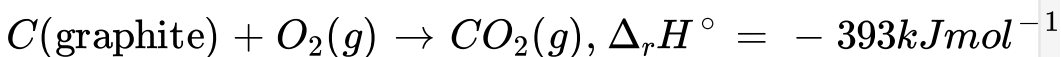
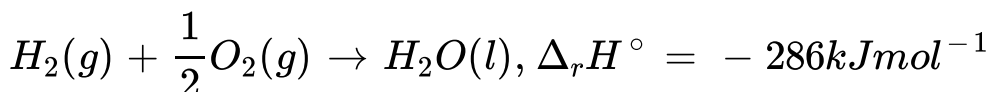
What is the standard enthalpy of formation of NH_3 gas ?

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53. From the following data



$$\Delta_r H^\circ = -726 \text{ kJ mol}^{-1}$$

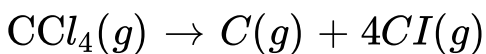


The standard enthalpy of formation of $CH_3OH(l)$ in kJ mol^{-1} is



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54. Calculate the enthalpy change for the process



and calculate bond enthalpy of $C - Cl \in CCl_4(g)$.

$$\Delta_{\text{vap}} H^\theta (C Cl_4) = 30.5 \text{ kJ mol}^{-1}.$$

$$\Delta_f H^\theta(\text{Cl}_4) = -135.5 \text{ kJ mol}^{-1}.$$

$\Delta_0 H^\theta(C) = 715.0 \text{ kJ mol}^{-1}$, where $\Delta_a H^\theta$ is enthalpy of atomisation.

$$\Delta_a H^\theta(\text{Cl}_2) = 242 \text{ kJ mol}^{-1}.$$



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55. For an isolated system, $\Delta U = 0$ what will be ΔS ?



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56. For the reaction at 298 K,



$$\Delta H = 400 \text{ kJ mol}^{-1} \text{ and } \Delta S = 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}.$$

At what temperature will the reaction becomes

spontaneous considering ΔH and ΔS to be constant over the temperature range?



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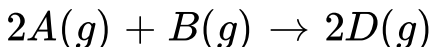
57. For the reaction,

$2Cl(g) \rightarrow Cl_2(g)$, what are the signs of ΔH and ΔS ?



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58. For the reaction,



$$\Delta U^\theta = -10.5 \text{ kJ} \text{ and } \Delta S^\theta = -44.1 \text{ JK}^{-1}$$

Calculate ΔG^θ for the reaction, and predict whether the reaction can occur spontaneously or not.



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59. The equilibrium constant for a reaction is 10. What will be the value of ΔG ?

$$R = 8.314 JK^{-1}mol^{-1}, T = 300K.$$



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60. State the first law of thermodynamics. Explain its mathematical notation.



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61. State the second law of thermodynamics in any two ways.



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62. Explain Gibbs energy, enthalpy, entropy.



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63. Explain the spontaneity of a reaction in terms of enthalpy change, entropy change and Gibbs energy change.



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Long Answer Questions

1. State and explain the Hess's law of constant heat summation.



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2. Explain the experiment to determine the internal energy change of a chemical reaction.



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3. Explain the experiment to determine the enthalpy change of a chemical reaction.



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4. Explain the spontaneity of a reaction in terms of enthalpy change, entropy change and Gibbs energy change.



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Important Questions

1. Define a system. Give an example.



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2. The wall is adiabatic and $\Delta U = W_{ad}$. What do you understand about the heat and work with respect to the system?



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3. Express the change in internal energy of a system when
iii) w amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be?



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4. In isothermal free expansion of an ideal gas find the value of q and ΔU .



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5. In isothermal irreversible change of ideal gas what is the value of q ?



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6. In isothermal reversible change of an ideal gas, what is the value of q ?



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7. For an adiabatic change of in an ideal gas what is the relationship between its ΔU and $W(\text{adiabatic})$?



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9. What are the sign conventions of the work done on the system and work done by the system?



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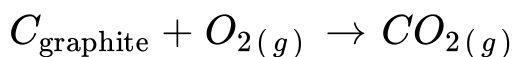
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11. What are intensive and extensive properties?



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12. 1 g of graphite is burnt in a bomb calorimeter in excess of O_2 at 298 K and 1 atm. Pressure according to the equations.



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13. What is $\Delta_r H$ for $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O(l)$ in terms of molar enthalpies of the respective reaction and products?



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14. Explain the relationship between Gibbs energy change and equilibrium constant.



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15. State the third law of thermodynamics.



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16. What are open, closed and isolated systems ? Give one example for each.



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17. Define the state function and state variables. Give examples.



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18. "Internal energy is a state function." Explain.



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19. "Work is not a state function." Explain.



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20. Explain the state function 'enthalpy, H '. What is the relationship between ΔU and ΔH ?



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21. Explain extensive and intensive properties.



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22. Define heat capacity. What are C_p and C_v ? Show that

$$C_p - C_v = R.$$



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23. Explain the determination of ΔU of a reaction calorimetrically.



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24. Explain the determination of ΔH of a reaction calorimetrically:



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25. What is enthalpy of a reaction? Explain the standard enthalpy of a reaction.



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26. What is the standard enthalpy of formation? Explain it with example.



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27. Define and explain the enthalpy of combustion $(\Delta_c H^\theta)$.



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28. Define and explain the bond enthalpy $(\Delta_{\text{bond}} H^\theta)$.



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33. Which formulate in the following are correct?

a) $G = H - TS$

b) $\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$

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d) $\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \frac{(-\Delta H_{\text{sys}})}{T}$

e) $\Delta S_{\text{total}} = T\Delta S_{\text{sys}} - \Delta H_{\text{sys}}$



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34. State the third law of thermodynamics.



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35. Explain the mole concept.



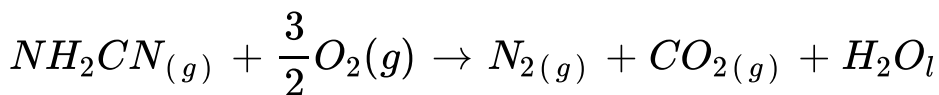
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